



# Optimisation of the variational method for vibrational Hamiltonian eigenvalues computation

Romain Garnier, Vincent Le Bris, Didier Bégué, Olivier Coulaud, Isabelle Baraille, Marc Odunlami

## ► To cite this version:

Romain Garnier, Vincent Le Bris, Didier Bégué, Olivier Coulaud, Isabelle Baraille, et al.. Optimisation of the variational method for vibrational Hamiltonian eigenvalues computation. 59th Souriau Colloquium: Colloque International de Théories Variationnelles, Jun 2015, Seignosse, France. hal-01179654v2

**HAL Id: hal-01179654**

**<https://hal.science/hal-01179654v2>**

Submitted on 14 Oct 2015

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Optimisation of the variational method for vibrational Hamiltonian eigenvalues computation

Romain Garnier <sup>\*</sup>    Vincent Le Bris <sup>†</sup>    Didier Bégue <sup>†</sup>    Olivier Coulaud <sup>\*</sup>  
 Isabelle Baraille <sup>†</sup>    Marc Odunlami <sup>†</sup>

April 23, 2015

## abstract

We propose here an efficient method to define a representative approximation subspace to compute the first eigenvalues of the vibrational Hamiltonian which are those of interest in the experimental results. In the Born Oppenheimer approximation, calling by  $\mathbf{x} = (x_1, \dots, x_N)$  the dimensionless normal coordinates [4],  $\omega_i$  the angular frequency associated with the coordinate  $x_i$  and  $\hbar$  the reduced Planck constant, the vibrational Hamiltonian  $\mathcal{H}$  writes as a sum of the nuclear kinetic and potential energies:

$$\begin{aligned} \mathcal{H}(\mathbf{x}) &= \mathcal{H}_0 + \mathcal{V} \\ &= \sum_{i=1}^N \frac{\hbar \omega_i}{2} \left( -\frac{\partial^2}{\partial x_i^2} + x_i^2 \right) + \sum_{S_V \geq \|\mathbf{s}\|_1 \geq 3} K_{\mathbf{s}} \prod_{i=1}^N x_i^{s_i}, \quad \mathbf{s} = (s_1, \dots, s_N). \end{aligned} \quad (1)$$

In (1) each monomial have a total degree  $\|\mathbf{s}\|_1 \leq S_V$ . The polynomial approximation of the potential energy is constituted by  $\mathcal{V}$  and the second order monomials included in  $\mathcal{H}_0$ .

The eigenfunctions of  $\mathcal{H}_0$  are pseudo-periodic signals vibrating at multiple level of fundamentals Harmonic frequencies. They write as

$$\phi_{\mathbf{n}}^0(\mathbf{x}) = \prod_{i=1}^N \psi_{n_i}(x_i), \text{ for all } \mathbf{n} = (n_1, \dots, n_N), \psi_{n_i}(x_i) \text{ Hermite function of degree } n_i. \quad (2)$$

And the harmonic corresponding eigenvalues of  $\mathcal{H}_0$  are

$$E_{\mathbf{n}}^0 = \sum_{i=1}^N \left( n_i + \frac{1}{2} \right) \omega_i \hbar. \quad (3)$$

Variational method in quantum mechanic is used to design a method that uses an adapted set of trial wave functions defining a subspace where the eigen-pairs of  $\mathcal{H}$  are computed.

---

<sup>\*</sup>INRIA Bordeaux

<sup>†</sup>IPREM Pau

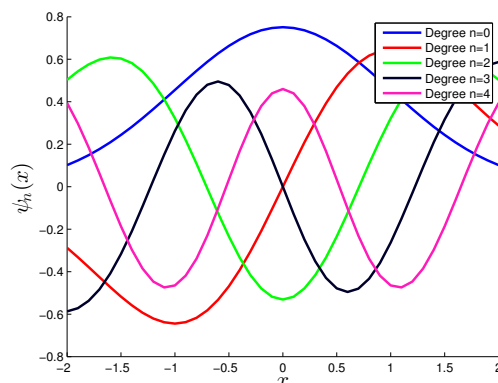


Figure 1: First hermite functions from degree 0 to 4

The eigenfunctions of  $\mathcal{H}_0$  (2) constitute a well-suited approximation space. Indeed, when looking at the form of the operator  $\mathcal{H}$  (1) we see that  $\mathcal{H}_0$  already contains Kinetic energy and the quadratic terms of the potential energy faithfully representing its behaviour in a localized area around equilibrium. In other words,  $\mathcal{H}_0$  is the zero order approximation of  $\mathcal{H}$ .

In order to deal with the curse of dimensionality that rapidly Happens because of the product space structure of the approximation space, we propose a basis selection technique based on perturbational theory [3].

This technique is in the context of vibrational configuration interaction with perturbation selected interactions [2, 1].

Calling by  $\|\mathcal{V}\|_2$  the spectral norm of the operator  $\mathcal{V}$ , the first eigenvalues of  $\mathcal{H}$  are considered perturbation of the first harmonic eigenvalues because

$$\|\mathcal{V}\|_2 = \epsilon * \|\mathcal{H}_0\|_2, \quad \epsilon < 1. \quad (4)$$

Actually, the value of  $\epsilon$  depends on the distance with the ground state and then constitute relevant information for the selection of the minimal required sub basis for the computation of the eigen-pairs of  $\mathcal{H}$ .

## References

- [1] I. Baraille, C. Larrieu, a. Dargelos, and M. Chaillet. Calculation of non-fundamental IR frequencies and intensities at the anharmonic level. I. The overtone, combination and difference bands of diazomethane,  $\text{H}_2\text{CN}_2$ . *Chemical Physics*, 273:91–101, 2001.
- [2] Didier Bégué, Neil Gohaud, Claude Pouchan, Patrick Cassam-Chenai, and Jacques Liévin. A comparison of two methods for selecting vibrational configuration interaction spaces on a heptatomic system: Ethylene oxide. *Journal of Chemical Physics*, 127, 2007.
- [3] J. J. Sakurai. *Modern Quantum Mechanics*. 54:668, 1986.
- [4] E B Wilson, J C Decius, and P C Cross. *Molecular Vibrations: The Theory of Infrared and Raman Vibrational Spectra*. Dover Books on Chemistry Series. Dover Publications, 1955.